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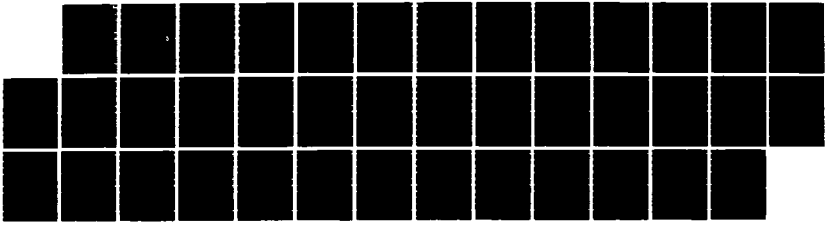

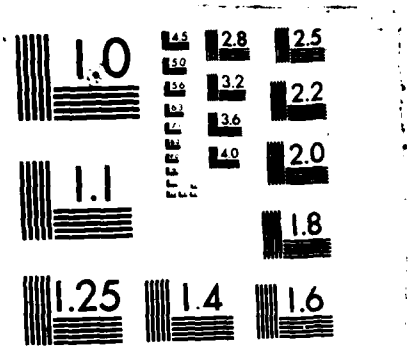

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The preparation, characterization and application of electrodes with specific chemical properties that are imparted by surface modification with polymer networks are the long-range goals of this research. Networks that are formed by crosslinking with gamma radiation have been evaluated with respect to swelling in aqueous solution, retention of polymer in the network, permeability, and the effect

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20. ABSTRACT continued

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of radiation dosage on all of these properties through its control of crosslinking. Ionic water-soluble polymers such as poly[diallyl dimethyl ammonium chloride], poly[vinylbenzyl trimethyl ammonium chloride], poly[styrene sulfonic acid, sodium salt] and poly[acrylic acid], which would ordinarily dissolve from the electrode surface in aqueous solution unless crosslinked into a network, and several neutral polymers such as poly[acrylonitrile], poly[ethyleneimine], poly[dimethylsiloxane] and poly[vinyl alcohol] have been investigated. The covalent attachment of organic and inorganic redox mediators and enzymes to networks by gamma irradiation of a mixture of polymer and the agent have been investigated. Network-coated electrodes with the appropriate properties are being developed for specific applications that require a stable, easily fabricated, fouling-resistant, rapidly responding, sensitive, and selective electrode.

PREPARATION, CHARACTERIZATION, AND UTILIZATION OF ELECTRODES COATED WITH POLYMERIC NETWORKS FORMED BY GAMMA RADIATION CROSSLINKING

FINAL REPORT

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U. S. ARMY RESEARCH OFFICE

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UNIVERSITY OF CINCINNATI

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ABSTRACT

The preparation, characterization and application of electrodes with specific chemical properties that are imparted by surface modification with polymer networks are the long-range goals of this research. Networks that are formed by crosslinking with gamma radiation have been evaluated with respect to swelling in aqueous solution, retention of polymer in the network, permeability, and the effect of radiation dosage on all of these properties through its control of crosslinking. Ionic water-soluble polymers such as poly [diallyl dimethyl ammonium chloride] , poly [vinylbenzyl trimethyl ammonium chloride], poly [styrene sulfonic acid, sodium salt] and poly [acrylic acid], which would ordinarily dissolve from the electrode surface in aqueous solution unless crosslinked into a network, and several neutral polymers such as poly [acrylonitrile], poly [ethyleneimine] , poly [dimethylsiloxane] and poly [vinyl alcohol] have been investigated. The covalent attachment of organic and inorganic redox mediators and enzymes to networks by gamma irradiation of a mixture of polymer and the agent have been investigated. Network-coated electrodes with the appropriate properties are being developed for specific applications that require a stable, easily fabricated, fouling-resistant, rapidly responding, sensitive, and selective electrode.

I. Background

A. Significance of Chemically Modified Electrodes

Research activity in the area of chemically modified electrodes (CMEs) has increased dramatically in the past few years (1-5). Modification involves the immobilization of a molecular species on the electrode surface and permits the tailoring of a surface for application to a specific problem in synthesis, analysis, electrocatalysis, stabilization of semiconductors, photosensitization, energy conversion, or photochromic displays.

Examples of modified electrodes for selective synthesis include graphite electrodes with optically active amino acids bound to surface oxides for asymmetric reduction of ketones to optically active alcohols (6), an α-cyclodextrin

chemically modified graphite electrode for regio-selective anodic chlorination of some benzene derivatives (7), and polymeric metalloporphyrin coated electrodes for selective reduction of oxygen to hydrogen peroxide or water (8).

Polymer-modified electrodes have demonstrated utility as selective and sensitive preconcentrating surfaces for electroanalysis (9-11). Ligands bound to pyrolytic graphite as polymers concentrate metal ions at the surface from dilute solutions (4, 12-14). A new class of macrocyclic metal chelators (15) may prove useful for such applications. Extension of this approach to the determination of organic compounds (10, 16) indicates the potential analytical applications of CMEs.

CMEs exhibit electron-mediated electrocatalysis for a variety of substances. Redox mediator-catalysts immobilized at electrode surfaces allow electrochemical detection of biologically-derived redox systems which ordinarily exhibit slow electron transfer kinetics at unmodified surfaces (17). Development of such mediator schemes should make feasible the analysis and investigation of biological redox systems not readily observed at unmodified electrode surfaces. Voltammetric (18, 19) and potentiometric (20, 21) responses for several biological couples have also been observed at electrodes coated with polymer films alone (i.e. no immobilized electron-transfer mediator required). Other examples of reactions whose rates are accelerated at modified electrode surfaces are reduction of oxygen (22-25) and oxidation of ascorbic acid (26-30).

Another currently active and exciting area of research involves enzyme (or substrate) immobilization on electrode surfaces. Many of these studies entail immobilization of glucose oxidase and monitoring of the reaction by differential pulse voltammetric (31), amperometric (32, 33), or potentiometric (34) techniques.

The potential importance of CMEs in such diverse areas of application has projected this particular area of electrochemistry to the forefront of the field in terms of research activity.

B. Background on Chemically Modified Electrodes

1. **General.** Three general methods for immobilizing species on electrode surfaces have been developed (4, 35).

(a) **Covalent bonding** of the species to functional groups on the electrode surface - This method often involves attachment of organosilanes to metal oxide surfaces bearing other reactive chemical or electrochemical functionalities. Examples are silanization with subsequent quaternization (36);

coordination to metals (37, 38); coupling as amides through reaction with amines (39, 40), acid chlorides (41-49), or carboxylic acids (38, 42, 43, 47, 50-57); and subsequent coupling as sulfonamides through reaction with sulfonyl chlorides (55, 58, 59). Other techniques include attachment of monomers as esters to metal oxides (35) and attachment of monomers to carbon oxides by coupling with amines or alcohols (6, 50, 60-66).

(b) **Chemisorption** (or "irreversible" adsorption) of the reagent on an electrode surface -- examples are olefins adsorbed on platinum (67, 68); molecules with extended π-systems adsorbed on graphite (69-72); amines adsorbed on platinum (35).

(c) **Polymer films** bonded to or coated on an electrode surface -- examples are given below in Section 2.

The development of chemically modified electrodes has been reviewed twice by the principal investigator (1, 2), twice by Murray (4, 5), and by Snell and Keenan (3). Since this proposal deals with polymers as the means of surface modification, this mode of surface immobilization on an electrode is detailed in the next section.

2. Polymer-Coated Electrodes. Numerous research groups have explored the concept of coating an electrode surface with a polymer film. Polymer coatings as a medium for immobilizing reagents on an electrode surface are potentially advantageous in several respects (2, 4, 5, 35). The immobilization of a polymer film is usually easier technically than covalent attachment of monolayers. Since polymer films are usually multilayers, electrochemical and spectroelectrochemical responses are much larger than for covalently attached or adsorbed monolayers, a feature that facilitates characterization. A polymer network can serve as a convenient framework for the introduction of functional groups. In the case of electrocatalysis, theory shows that multilayers are better than monolayers (73). Different polymer films may be "layered" to obtain specific properties such as a charge rectifying interface (74-77). Electrode-immobilized polymers can function as permselective membrane electrodes for use as fouling-resistant, selective, and sensitive electrochemical sensors (78).

An important component of the research on polymer-coated electrodes has been the search for suitable polymers for coating various types of electrodes and the development of different ways to effect polymerization on an electrode surface. Immobilization techniques have involved dip coating (79-88), spin coating

(81, 89-91), electrochemical deposition (21, 75, 76, 92-100), adsorption from solution (101-104), plasma discharge polymerization (30, 105, 113), organosilane bonding (77, 114-125), and (in the principal investigator's laboratory) formation of cross-linked polymer networks through gamma irradiation (126).

Numerous polymers have been coated on electrodes: polyvinylpyridine (79, 80, 101-103, 127, 128); quaternized polyvinylpyridine (129); polyvinyl sulfate (129); ferrocene polymers such as polyvinylferrocene (92, 93, 107), poly(vinylferrocene acrylonitrile) (93), and poly-5- ferrocenylethylamine (104); polyacrylonitrile (101, 102, 130); polyacrylic acid (79); polymethacryl chloride (81, 114); functionalized polystyrenes (82, 89, 129, 131); polyazobenzene (132); polyaniline (94); poly-1,2-diaminobenzene (21); polymers of anthraquinone (83); polymerized monosubstituted aromatic amines (95); polyphenylene oxide with amine functions (96); silane polymers (115); and polyacetylene (133). These polymer films have been coated on a variety of substrates: pyrolytic graphite (79, 101-104, 106, 128, 129), glassy carbon (81, 130, 132), platinum (21, 82, 89, 92-96, 107, 115, 127, 130, 131), tin oxide (114), iron (96), copper (96), and mercury (83, 132).

A significant aspect of the research reported thus far on polymer-coated electrodes has been the study of electroactive groups in the polymer matrix. Such electroactive groups have been incorporated in the coating as electroactive components in the monomer [e.g., polyvinylferrocene (92), poly-p-nitrostyrene (82), "functionalized" polystyrenes (89)], covalent attachment of an electroactive species into a polymer already coated on an electrode [e.g., covalent attachment of electroactive hydroxymethylferrocene to SnO_2 coated with poly(methacryl chloride)(114)], extraction of an electroactive species into a charged polymer film (polyelectrolyte) due to electrostatic attraction [e.g., $Fe(CN)_6^{3-}$ and $IrCl_6$ into polyvinylpyridine (as a cationic film) (79); $Ru(NH_3)_6^{3+/2+}$ into polyacrylic acid (as an anionic film) (134); $Fe(CN)_6^{3-}$ into quaternized polyvinylpyridine (11); $Ru(bipy)_3^{2+}$, $Co(bipy)_3^{3+}$, $Co(phen)_3^{3+}$ and $Ru(NH_3)_6^{3+}$ into polyvinyl sulfate, polystyrene sulfonate and polyacrylic acid (135)], or complexation with an immobilized ligand [e.g. Ru(III) EDTA and $Ru(NH_3)_5$ complexes coordinatively attached to pyridine in polyvinylpyridine (101)]. The study of these electroactive groups by electrochemical techniques such as cyclic voltammetry has given valuable information concerning the mechanism of "charge transport" [electron transfer (108, 109) through a redox polymer film (99, 108, 109, 136-143)] and the effects of various

properties of the polymer (e.g., swelling in solvent, permeability to ions, electronic conductivity, and internal mobility). At present, the actual mode of transport of electrochemical charge through polymer films remains unsettled, but this area is being actively investigated by a number of workers (84, 90, 91, 99, 108, 109, 136, 138-162). Current discussion of this issue considers roughly three major categories (5):

(a) electron transport mechanism in the polymer film (108, 136-139, 141, 152);

(b) influence of counterion transport (144, 154, 159) and segmental polymer chain motions (108, 139) as possible rate-determining steps (as opposed to rate of electron exchange between neighboring oxidized and reduced sites) in the electron transport mechanism; and

(c) dependence of charge transport on electroactive site concentration (also a possible factor involved in the rate-determining step)(141-143, 145, 146, 148, 150, 153, 155, 157-164).

In a few instances, polymer-coated electrodes have been successfully used to catalyze reduction/oxidation of a substrate [e.g., O_2 reduction (22-25); ascorbic acid oxidation (26-30)]. Further investigation of the above areas will provide important information for the design of polymer electrodes for specific applications.

C. Conclusions

Although the use of polymers to modify electrodes for specific applications is an active research area, little work has been done to systematically evaluate the effects of cross-linking agents (gamma radiation, UV-radiation, chemical agents, etc.) on important properties of the polymer film such as stability, adhesion to the electrode surface, and permeablity to solution species. Cross-linking techniques are used extensively in the field of polymer chemistry such as in the development of elastomers and thermosetting resins; however, the existing cross-linking methodology has been underutilized for the development of polymer coated electrodes (87, 126, 127, 130). In addition to formation of durable immobilized polymer coatings, cross-linking techniques offer potential means of stable incorporation of functional groups (such as chelons, enzymes, or redox catalysts) through covalent bonding (versus electrostatic trapping) to the polymer network.

In this research project we have explored the use of carefully controlled cross-linking techniques (primarily gamma irradiation) for control of the polymer network structure including variation in permeability (achieved by polymer crosslinking, degradation, or both) and introduction of specific functional groups in order to produce polymer coated electrodes with desirable chemical properties.

D. Crosslinking with Gamma Radiation

Gamma radiation generates free radicals on polymer chains which react to covalently cross-link the chains into a continuous network. Network formation insolubilizes polymers. If, however, the uncross-linked polymer was soluble in the medium to be used for the electrochemical measurement, the cross-linked network will swell when placed in contact with that medium. Such a swollen network has a very open structure, the permeability of which can be controlled by changes in the cross-link density.

Gamma irradiation has several advantageous features as a technique for cross-linking. It is a technique which cross-links many different polymers and consequently should be a general method for forming polymer-coated electrodes. Different radiation doses can be used to control the degree of cross-linking and thus the permeability of the electrode to various solution species. For polymers of the crosslinking type, an incease in radiation dose should generate a greater population of free radicals and therefore result in more cross-links up to the dose where all crosslinking sites are exhausted and degradation processes predominate. Gamma radiation is a good source for generating free radicals due to its ability to penetrate the polymer layer and produce a homogeneous distribution of radical sites. Another free radical source, UV radiation, can exhibit limited film penetration and can require the addition of free-radical initiators. Chemical means of free-radical generation rely on the mass transfer of the radical generator into the polymer matrix and require the ability to completely remove the chemical additive and by-products once the reaction is finished. Of these three methods for generating free radicals, gamma radiation is best suited as a general method for creating a homogenous distribution of cross-links in a polymer film on a surface such as an electrode.

II. Progress Report

A. Objectives

The specific objectives for the funding period covered by this report (8/1/82 - 1/31/87) were as follows:

(a) Determine if the formation of polymer networks by gamma-radiation cross-linking is a viable technique for the preparation of polymer-modified electrodes. Investigate several types of polymers for the purpose of evaluating the general applicability of this approach. Ionic polymers that are water-soluble are of special interest since the formation of a network should render the film insoluble in water, thereby enabling the resulting polymer-modified electrode to be used in this medium.

(b) Characterize the resulting polymer electrodes with respect to a number of features such as swelling, charge attraction and repulsion, electrochemical properties, and effects of variation in radiation dosage.

(c) Determine if variation in cross-link density can be used to control permeability of the film.

(d) Determine if redox agents and other specific functional groups can be incorporated into a polymer electrode by covalent attachment during irradiation. Characterize the resulting electrodes with respect to efficiency of incorporation and chemical state of the incorporated group.

(e) Determine if network-modified electrodes can be used in a practical sense for prevention of electrode fouling by controlling access to the substrate surface or for catalysis of analytically important species.

B. Polymers Examined

A variety of polymers has been investigated, each for its amenability to the formation of networks on electrode surfaces by gamma-radiation crosslinking. The polymers and their structures are shown in Table 1. All of these have been found to form cross-linked networks when exposed to gamma radiation. The network films adhere to conductive substrates such as graphite, platinum, and gold, which enables the successful preparation of modified electrodes. Since all of the polymers that have been investigated thus far were successfully cross-linked by gamma irradiation, it seems likely that this is a general technique for preparing polymer modified electrodes. Additional polymers need to be tested to further substantiate this assertion.

C. Electrode Preparation

Of the several procedures for preparing the electrodes that were tried, the following simple procedure worked well in most cases. Appropriate amounts of polymer (and redox agent, when applicable) were dissolved in water, and either one or more aliquots of this solution were applied to the electrode with a micropipet or the electrode was dipped in the solution. Electrodes were then dried by spinning in a stream of warm air. If multiple aliquots were applied, each coat was dried before the next coat was applied. Once a batch of electrodes had been prepared and all the solvent removed by drying, the electrodes were treated to three cycles of a vacuum evacuation/argon purge, transferred to the interior of an argon-filled glove box, and packed individually in 2-dram glass vials that were then placed inside of glass jars. Both jars and vials were screw-sealed with parafilm forming a gasket. Failure to remove oxygen resulted in poor network formation, since oxygen is an effective free radical trap. Next, the electrodes were irradiated at the Phoenix Memorial Laboratory, Ford Nuclear Reactor, University of Michigan, Ann Arbor, where they received dosages varying from 0.01 to 15 Mrad. Before electrochemical evaluation, the electrodes were soaked in continually renewed 0.5 M NaCl solution to remove unattached redox species and polymer.

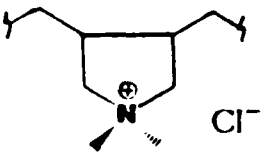
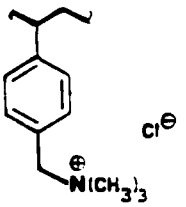
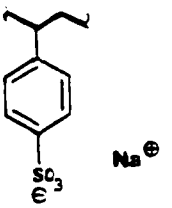
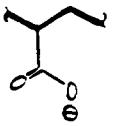
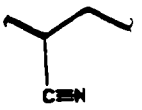
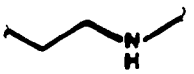
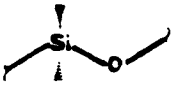
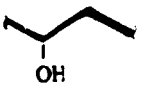
D. Effects of Gamma Irradiation on a Water-Soluble Polymer: DDAC

Four water soluble polymers were investigated -- DDAC, VTAC, PSSASS and PAA. All four polymers formed cross-linked networks on electrode surfaces when exposed to gamma radiation. The resulting films were insoluble in water and adhered to the electrode substrate. Results of experiments on DDAC are representative and are summarized below.

Properties of DDAC cross-linked by gamma radiation were first determined on samples of DDAC in the form of polymer strips that were not attached to an electrode.

Cross-linked DDAC was found to swell ca. 1.5x when immersed in 0.5M NaCl. No significant change in swelling occurred with variation in radiation dosage (0.01 to 8.0 Mrad), which suggests that these dosages produce the maximum cross-link density. Apparently cross-linking of DDAC can be achieved with very low dosages. The specific volume, which is the ratio of the swollen volume to the mass of dry polymer sample, was found to be 1.4 mL/g in 0.5 M NaCl. This number enables the volume of swollen polymer on an electrode to be calculated from the amount of dry

Table 1. Polymers

name	abbreviation	structure	mol wt
poly [diallyl dimethyl ammonium chloride]	DDAC		$2.5 - 30 \times 10^5$
poly [vinylbenzyl trimethyl ammonium chloride]	VTAC		
poly [styrene sulfonic acid sodium salt]	PSSASS		3×10^6
poly [acrylic acid]	PAA		$2 - 6 \times 10^3$
poly [acrylonitrile]	PAN		1.5×10^5
poly [ethyleneimine]	PEI		1.8×10^3
poly [dimethysiloxane]	PDMS		$0.5 - 100 \times 10^3$
poly [vinylalcohol]	PVAL		$3 - 125 \times 10^3$

polymer applied to the substrate. Most of the results described here were on ca. 5 u-thick films.

E. Electrochemistry of DDAC Networks on Platinum and Graphite

Electrodes discussed in the following sections are described by the notation: gamma^{D}-S;P, where D is the radiation dose, S the electrode substrate, and P is the immobilized polymer network.

A cyclic voltammogram of a gamma^{8}-graphite;DDAC electrode in supporting electrolyte exhibits only residual current. As expected for a film composed primarily of a quaternary ammonium ion-based polymer, no voltammetric waves due to faradaic processes are observed. Similar behavior was observed for the other ionic polymers.

Approximately half of the DDAC applied to a gamma$^{0.25}$-graphite;DDAC electrode was retained on the electrode surface after soaking in stirred 0.5 M NaCl for 48 h. The polymer lost from the film presumably consists of DDAC chains that were not cross-linked to the network by irradiation. The remaining film of polymer network was found to always adhere tightly to graphite substrate. In the case of platinum, however, the DDAC network sometimes parted from the substrate. Immobilization is apparently due to insolubilization of a cross-linked network and the suspected formation of substrate/polymer bonds that are important for retaining the film on the substrate. The tenacity with which films adhere to graphite is consistent with the network having been covalently bonded to the graphite surface by the irradiation process. Graphite porosity is also a probable contributor to film retention in that polymer-filled pores could serve to anchor the network to the electrode surface.

Networks of DDAC and the other ionic polymers were found to be permeable to solution redox species such as ferricyanide as evidenced by the cyclic voltammograms in Figure 1. The peak heights of voltammograms of bare and coated electrodes show almost identical current levels. At the 5Mrad dosage level a film such as this (approximately 5 microns thick) has a relatively open structure when swollen. Cyclic voltammograms on electrodes exposed to varying doses of radiation were essentially identical. Thus, the permeability of DDAC films of this thickness cannot be controlled by the cross-linking dosage within the range employed here. This behavior is consistent with the insensitivity of polymer swell to radiation dose mentioned earlier.

The nature of the supporting electrolyte influences the electrochemistry of ferricyanide as shown by cyclic voltammograms of ferricyanide at a gamma[1]-Pt;DDAC electrode in the supporting electrolyte anions HSO_4^-, NO_3^-, and Cl^-. A supporting electrolyte anion that is more strongly bound to the network would be expected to compete with ferri-ferrocyanide for charge sites in the network. Binding strengths of anions are qualitatively given as 'selectivities' when considering cross-linked resins for ion exchange chromatography. For the quaternary ammonium resin Durrum DA-XAF, which is somewhat similar to cross-linked DDAC, the selectivity is as follows: $HSO_4^- > NO_3^- > Cl^- > OAc^- > OH^-$(165). The peak heights of cyclic voltammograms showed a correlation with these selectivities. Peak height increases in the order $HSO_4^- < NO_3^- < Cl^-$ as ferri-ferrocyanide competes more effectively with the supporting electrolyte anion.

Ferri-ferrocyanide partitions into the DDAC film with repetitive cycling. Cycling gave increasing peak current (Figure 2) until a steady state voltammogram (50 cycles) was obtained. Charge-trapped ferricyanide exhibits an apparent diffusion coefficient, D_{app}, [determined by chronocoulometry, (166)], of 3.9×10^{-9} cm^2/s. By comparison ferricyanide charge-trapped in protonated poly(4-vinyl pyridine) is reported to have a $D_{app} = 1.5 \times 10^{-9}$ cm^2/s (167). These values are substantially smaller than the diffusion coefficient observed at a bare electrode, 0.739×10^{-5} cm^2/s in 1.0M KCl (168). Electron transfer to the complex is impeded by either counter ion flow within the polymer, motions by the trapped complex, or cross electron exchange reactions (169).

The availability of ferri-ferrocyanide in the DDAC network to mediate electron exchange with redox species in solution was tested with cytochrome c. Immersion of a ferri-ferrocyanide-trapped gamma[0.25]-graphite;DDAC electrode in solutions of cytochrome c gives cyclic voltammograms with enhanced peak currents. An increase in current with cytochrome c concentration shows the mediation of electron transfer from the electrode to the cytochrome via the ferri-ferrocyanide. Electron transfer with a large biological molecule such as cytochrome c is apparently possible with redox mediators electrostatically trapped in cross-linked networks of this type.

F. Poly[acrylic acid] Films on Graphite: Charge Exclusion

Poly [acrylic acid] (PAA) is an example of a polymer whose charge can be

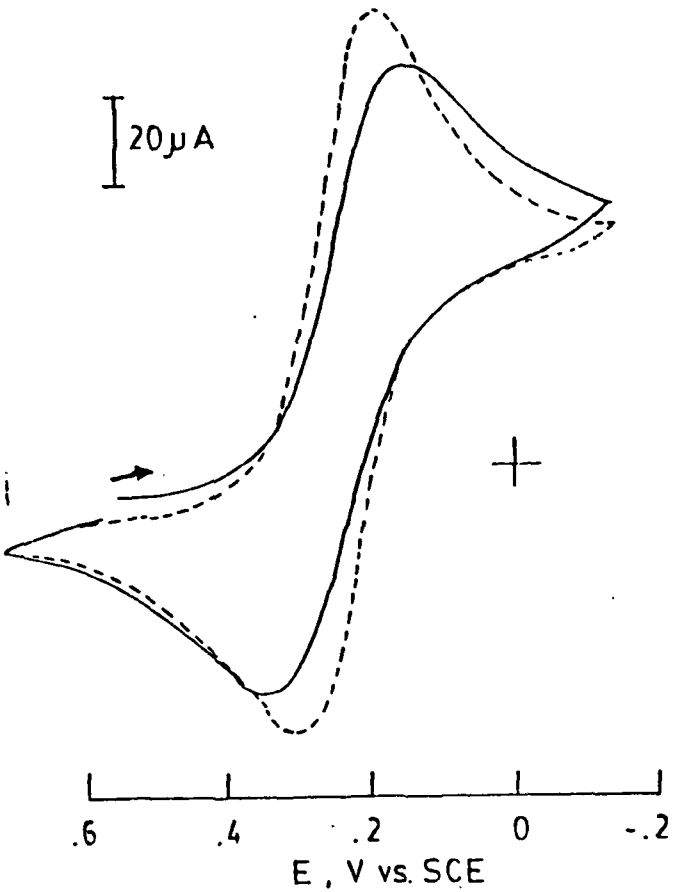


Figure 1. Cyclic voltammograms of (---) gamma^{5}-Pt;DDAC and (——) bare Pt in 4.0 mM $K_3[Fe(CN)_6]$. 0.5 M KNO_3. Scan rate, 10 mV/s.

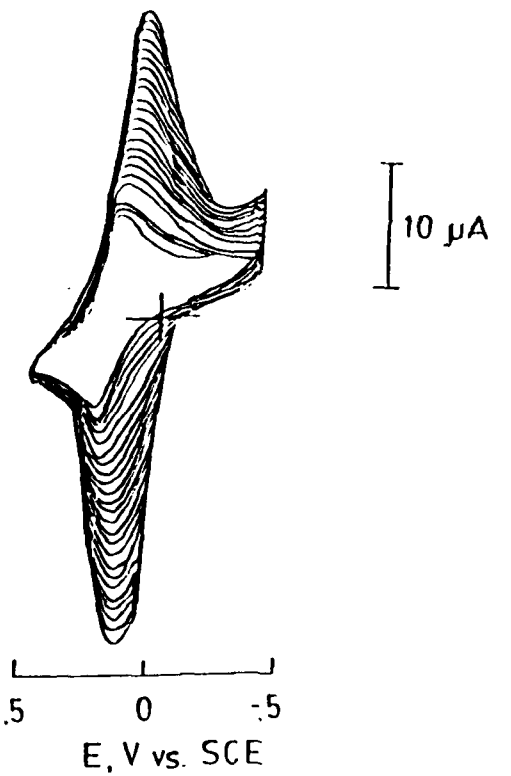


Figure 2. Cyclic voltammograms demonstrating charge trapping of ferricyanide in gamma^{15}-Pt;DDAC. Electrode cycled continuously at 20 mV/s in 0.5 mM $K_3[Fe(CN)_6]$, 1 M CH_3COONa, 2 M glycine, pH adjusted to 3.4 with HCl.

varied by the extent of protonation of the carboxylic acid functionality. Cyclic voltammograms of ferricyanide in solutions of different pH at a gamma$^{0.75}$-graphite;PAA electrode showed a marked (ca. 70%) decrease in the peak heights as the pH increased, which deprotonated the film. The negatively charged polymer inhibited the diffusion of the negatively charged ferricyanide anion to the electrode.

G. Poly[acrylonitrile] Networks on Gold: Size Exclusion

An interesting and potentially important property of gamma-radiation crosslinking is the ability to control, to a certain extent, the degree of crosslinking in the polymer film. A change in permeability should accompany a change in crosslinking as controlled by radiation dosage for certain polymers. The network film could then be used as a means of imparting size selectivity toward species in solution. This idea of size exclusion has been explored for other polymer systems (170-174).

Whereas the ionic polymers such as DDAC showed little variation in permeability with variation in radiation dose, neutral, water-insoluble polymers did. Poly [acrylonitrile] (PAN) on gold exhibited controlled access to the electrode surface (substrate metal) as a function of exposure to varying radiation dosage. Increased dosages caused greater attenuation of voltammetric waves for o-hydroquinone and ferricyanide up to ca. 1.0 Mrad, which cross-linked the polymer to the extent that no current was observable. Further exposure to gamma radiation caused film degradation as evidenced by an increasing voltammetric wave. Thus, gamma-radiation induced crosslinking and degradation may be an effective means of controlling permeability.

H. Poly[ethyleneimine] Networks on Platinum: Prevention of Electrode Fouling

A polymer film with characteristics of size selectivity is potentially useful for the purpose of preventing the fouling of electrode surfaces by strongly adsorbing species. This is particularly important in the analysis of biological samples such as blood plasma, which contains strongly adsorbing proteins. Since these proteins are comparatively large, an electrode coating that excludes large molecules but allows small molecules of analytical interest to pass would be useful. This idea was demonstrated with a poly [ethyleneimine] (PEI) network on platinum with ferricyanide in undiluted blood plasma. A bare Pt electrode showed immediate fouling of the electrode surface, whereas the PEI-modified electrode

resisted fouling by proteins as evidenced by essentially no change in this voltammogram during one hour's exposure to the plasma. Network films of this type apparently prevent the large proteins from reaching the electrode surface, whereas the smaller ferri-ferrocyanide can still be electrolyzed. This behavior is potentially very important in the development of biosensors for use in serum or other protein-containing samples.

I. Incorporation of Redox Catalysts

An important objective of this project has been to determine the feasibility of incorporating a specific molecule, such as an organic redox agent, into a polymer network by mixing it with the polymer prior to the irradiation step. The formation of free radicals by irradiation would result in covalent bonding of the redox molecule to the network as a result of the radical reactions. If successful, this procedure would provide an extremely simple technique for preparing electroactive polymer films. The concept has been demonstrated with 2,6-dichlorophenolindophenol (DCIP) in DDAC and o-hydroquinone in VTAC.

1. DCIP in DDAC. DCIP that is incorporated in a network of DDAC on an electrode is observable visually (the oxidized form is purple) and by cyclic voltammetry, as shown by curve A in Figure 3. By comparison, identically prepared electrodes that have not been cross-linked by irradiation lose the polymer film immediately when dipped in solution and, consequently, do not exhibit a voltammogram for DCIP as shown by curve B.

Evidence that the basic structure of electroactive DCIP in the DDAC network is minimally changed by the radiation procedure is given by the behavior of $E^{o'}$ with changes in solution pH. Plots of $E^{o'}$ (determined by cyclic voltammetry) versus pH for DCIP dissolved in solution compared to DCIP immobilized in a gamma$^{0.1}$-graphite; DDAC/DCIP electrode are in good agreement as shown in Figure 4. This suggests that the electrode mechanism for DCIP immobilized in a DDAC network is essentially the same as for DCIP dissolved in solution, namely a 2e, $2H^+$ reduction (175). The redox behavior of DCIP could be observed spectroelectrochemically for a DCIP/DDAC film coated on a platinum optically transparent electrode (126). Incorporated DCIP can be reversibly cycled between the colorless reduced form and the blue oxidized form by alternately stepping the potential between -0.200 V and +0.200 V. The electrochemical process is accompanied by a change in visible absorbance (ΔA) which can be measured. A

plot of ΔA as a function of wavelength (Figure 5) yields a maximum value at 560 nm, compared to the λ_{max} value of 610 nm reported for the solution species (175). The shift in wavelength is attributed to covalent linkage of the DCIP to the polymer network. The shift to shorter wavelength is consistent with the more positive $E^{0'}$ shown in Figure 4 for pH > 6. Covalent attachment to the polymer evidently stabilizes the oxidized form of DCIP.

Peak response to variation in scan rate was linear with respect to scan rate, ν, and non-linear with respect to $\nu^{1/2}$ over a range of 2 to 200 mV/s. This behavior is consistent with expectations for a redox species that is confined in a thin film (5). At scan rates greater than 200 mV/s ip vs. ν plots deviated from linearity whereas ip vs. $\nu^{1/2}$ plots became linear. Such mixed behavior has been reported for other polymer-coated electrodes and attributed to film resistance or "diffusion-like" motions of the electroactive species within the film, especially for thick films (173, 176-178).

"Apparent" diffusion coefficients (D_{app}) were calculated for the DCIP redox process. Since DCIP is attached to the network, the apparent diffusion coefficient is probably reflective of a concerted mechanism involving both polymer motion and counter ion diffusion (179). Apparent diffusion coefficients that were measured in different supporting electrolytes range from 0.45×10^{-7} cm^2/s in sulfate media to 1.7×10^{-7} cm^2/s in fluoride media. The apparent diffusion coefficients for DCIP electrochemistry in the DDAC film are about two orders of magnitude smaller than those for free DCIP (ca. 2.5×10^{-5} cm^2/s). Apparent diffusion coefficients of this magnitude have been observed for other polymer-film redox systems (5).

2. Retention of DCIP in the Network. Five types of DCIP can be postulated to exist in the polymer network after irradiation. (A) DCIP that is unreacted and consequently unattached to any polymer. This form of DCIP would be expected to rapidly leach out of the network when the electrode is immersed in a polar solvent which would be imbibed into and swell the network. (B) DCIP that is bonded to a polymer chain that is itself not attached to the network as a result of no cross-linking bond formation or chain scission. This form of DCIP would also be expected to leach out of the network if the polymer chain is able to "wiggle free". Leaching of this form might be slower than with free DCIP. (C) DCIP that is bonded to the network but which is sufficiently altered in structure due to the bonding reaction(s) as to be rendered electrochemically inactive. (D) DCIP that is bonded to the

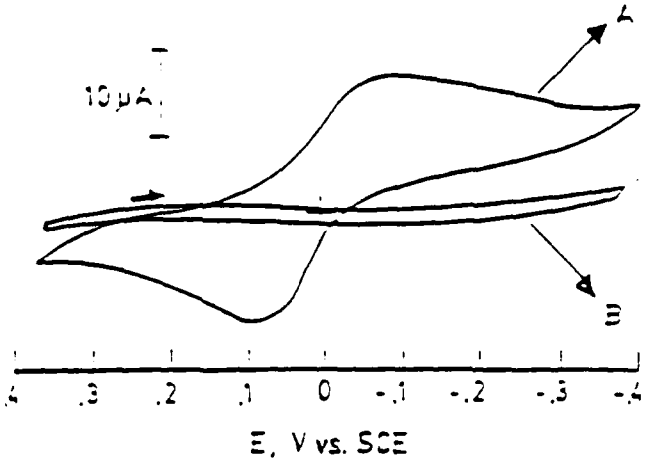


Figure 3. Cyclic voltammograms for platinum wires coated with a mixture of DDAC and DCIP. (A) Irradiated with a 1 Mrad dose, (B) Nonirradiated. Supporting electrolyte-0.1 M NaCl, 0.1 M phosphate buffer, pH=6.8. Scan rate 5 mV/s.

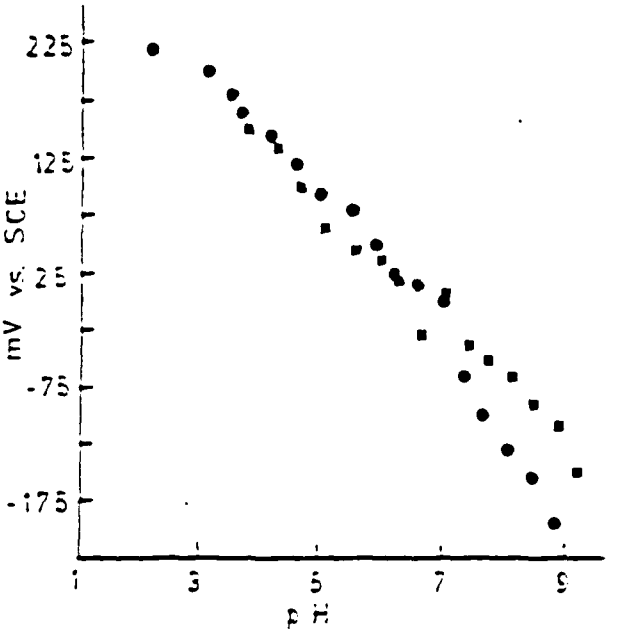


Figure 4. Formal reduction potential as a function of pH, ●-unmodified platinum wire in a solution of DCIP; ■ -gamma 0.1 - graphite/DDAC/DCIP,1:2.

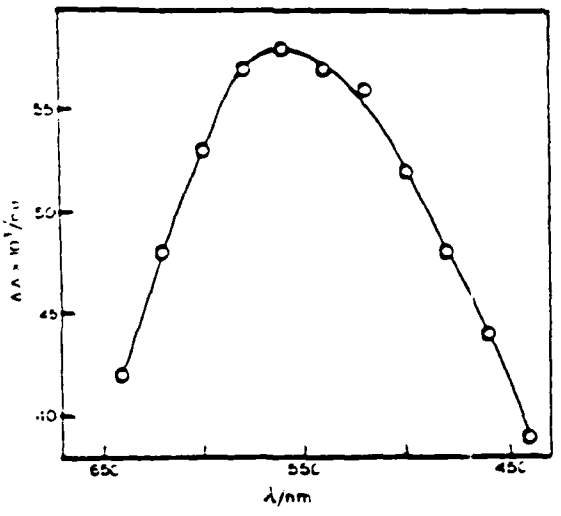


Figure 5. Absorbance change accompanying potential step from -0.200 V to +0.200 V vs. SCE, DCIP/DDAC-coated Pt OTE in 0.2 M KCl, pH 7.0 phosphate.

network, but which is physically inaccessible for electron transfer with the electrode (direct or indirect via electron exchange within the polymer film). These four types of DCIP would not be observable by cyclic voltammetry for an electrode that had been soaked to remove all "loose" material. (E) DCIP that is attached to the network, electroactive, and available for electron transfer with the electrode. This type, would be observable by cyclic voltammetry and related electrochemical techniques.

One objective of this study was to measure the distribution of DCIP among the various possible forms as a function of certain variables such as radiation dose, ratio of polymer to DCIP, and film thickness. In these experiments, the amount of electroactive DCIP (Type E) was measured by chronocoulometry; the amount of DCIP leaching from the film (Types A & B) measured spectrophotometrically on the leachate; and the amount of electroinactive DCIP (Types C & D) taken as the difference between (a) the known amount of DCIP originally in the polymer film and (b) the sum of the amounts found electrochemically and spectroscopically. These results are expressed in Tables 2, 3, and 4 in terms of the percentage of the *total DCIP originally present that remains bound* (electroactive & electroinactive) and the percent of the bound DCIP that is in an electroactive form, i.e., measurable by chronocoulometry.

The effect of dosage on % bound and % electroactive is shown in Table 2. The observed trend of increasing amount of species bound with increasing radiation dosage is to be expected. As the ionizing radiation dose increases, the number of free radicals increases, the number of bonds between DDAC chains to form the network increases, and DCIP-network bonds apparently grow in number. As the radiation level increases, the percentage of total bound DCIP that is electroactive decreases, although the <u>absolute</u> amount of electroactive DCIP remains essentially constant. Higher dosages either cause the attachment of more of the DCIP in an electroinactive configuration or the more highly cross-linked polymer inhibits molecular or ionic motions accompanying a successful electron transfer to the DCIP. Thus, although increased dosage enhances the <u>total</u> amount of DCIP attached to the network, the <u>relative</u> quantity that is <u>electroactive</u> decreases.

The ratio of amounts of polymer to redox molecule influences the % electroactive and % bound (Table 3). Except for the 1:1 ratio, the trend for % bound and % electroactive agrees with that in Table 2; more irradiation gives an

increasing amount of bound species of which the % electroactive decreases. Increasing the relative amount of DCIP in the DDAC to DCIP ratio progressively diminishes the fraction of DCIP that is electroactive.

As the electrode coatings become thinner, the % electroactive shows a slight increase. Table 4 compares three electrodes prepared with different amounts of DDAC-DCIP irradiated at the same dosage. Thinner films allow a somewhat larger percentage of the attached DCIP to participate in electron transfer, presumably since less of the redox species is positioned away from the electrode. The upper limit for film thickness appears to be on the order of 300 microns with the DDAC/DCIP system. Upon initial solvent imbibement, thicker films separate from the electrode substrate after swelling.

3. Swelling. DDAC/DCIP cross-linked sample strips placed in 0.5 M NaCl increase their volume by a factor of about 9 with no dependence on radiation dose (0.01 - 8.0 Mrad). This greater degree of solvent imbibement contrasts with the wet to dry polymer volume ratio of around 1.5 for the irradiated DDAC samples without DCIP. The presence of DCIP clearly causes additional swelling. Evidently bound DCIP decreases the cross-link density by inhibiting chain/chain bonds or structurally creating a more open network.

The specific volume for DDAC-DCIP is ca. 5 mL/g. Based on these values, typical thicknesses of swollen films of DDAC-DCIP on electrodes used in this report vary from 9 to 250 microns, depending on the amount of polymer applied .

J. Longevity.

The network electrodes prepared by gamma irradiation are reasonably durable. Electrodes have been used intermittantly for periods of over four months with a total in-solution time of 60 hours. Peak heights of cyclic voltammograms of DDAC/DCIP modified electrodes gradually decreased to about 40% of the original response over this time period.

K. Electron-Transfer-Mediated Electrocatalysis

An important objective of this phase of the project was to determine whether or not networks that are prepared by gamma-radiation crosslinking can be used for electron-transfer-mediated electrocatalysis. Two systems have been evaluated: DCIP in DDAC or VTAC for the reduction/oxidation of cytochrome c and o-hydroquinone in VTAC for the oxidation of nicotinamide adenine dinucleotide (NADH).

Table 2 Effect of Dosage on DCIP in DDAC for Graphite; DDAC/DCIP, 3:1 Electrode

dose (Mrad)	% bound	% electroactive	actual coverage $x10^8$ moles/cm^2
0.1	4	15	5.3
0.25	5.8	5.8	5.6
0.75	6.4	7.8	4.7
2.0	17	4.1	6.6
8.0	23	1.9	4.0
15	60	1.5	8.4

Table 3 Effect of DDAC: DCIP Ratio on % Bound and % Electroactive for Graphite; DDAC/DCIP Electrode

	% bound (DDAC : DCIP)				% electroactive (DDAC : DCIP)			
dose (Mrad)	10:1	3:1	2:1	1:1	10:1	3:1	2:1	1:1
0.25	21	8.1	5.3	38	6.5	6.3	3.0	0.27
2.0	31	15	53	38	2.3	3.5	0.19	0.70
8.0	45	25	62	---[a]	2.6	1.1	0.04	---[a]

[a] --- no experiment

Table 4 Effect of Film Thickness on DCIP in DDAC for Gamma$^{0.25}$-Graphite; DDAC/DCIP, 3:1 Electrode

film thickness, microns	% electroactive
140	12
65	15
10	19

1. DDAC/DCIP Catalysis of Cytochrome c. DCIP has been shown to mediate electron transfer to cytochrome c by homogeneous electron transfer in solution (175). Cytochrome c is only marginally reactive at certain unmodified electrodes (175), depending on the surface condition of the electrode (180). Figure 6 shows cyclic voltammograms of cytochrome c at a DDAC/DCIP-modified electrode. Distinctive cathodic and anodic waves show that cytochrome c is a chemically reversible couple at this electrode. The peak heights (corrected for the DCIP component of the current) are proportional to cytochrome concentration. No waves for cytochrome c were observed for a DDAC coated electrode without DCIP.

Gold minigrid has been modified with DDAC/DCIP and used for a thin-layer spectroelectrochemical study of cytochrome c. $E^{o'}$ values for cytochrome c were in good agreement with those reported for spectroelectrochemistry with solution-soluble mediators. No spectral interference from the surface-confined mediator was observed.

2. VTAC/o-hydroquinone Catalysis of NADH. Another example of electrode modification through immobilization of a polymer/redox molecule mixture is o-hydroquinone bonded to a VTAC network on graphite. Quinones are known to catalyze the oxidation of NADH (181,182). A cyclic voltammogram of the VTAC-hydroquinone electrode is shown in Figure 7. Addition of 2 mM NADH gives an increase in current with a redox potential for the oxidation of NADH shifted negatively about 200 mV from oxidation at an unmodified electrode (compare Figure 7B to 7C). This shift in potential correlates well with that observed on other quinone modified electrodes with vitreous carbon (181) and glassy carbon (182) substrates.

L. Electrochemical Oxygen Sensor with Polymer Coating

The Clark oxygen electrode is a commonly used device for the determination of oxygen (183). The electrode consists of a conducting metal such as platinum and a reference electrode that are mounted behind a thin membrane with a thin layer of electrolyte sandwiched between the membrane and the electrodes. Oxygen in the sample diffuses through the membrane and the electrolyte layer to the metal electrode where it is detected by reduction. A key feature of the electrode is the membrane which separates the electrode from the sample solution. The membrane imparts excellent selectivity for oxygen by allowing only gaseous species to pass

through. This also protects the electrode surface from fouling by preventing surfactants and other adsorbing species from reaching the surface.

Although remarkably successful, the Clark oxygen electrode has the disadvantage of somewhat slow response caused by the distance through the membrane and quiescent electrolyte layer that oxygen must diffuse to reach the electrode surface. Secondly, the electrode is difficult to easily miniaturize using the conventional membrane - spacer construction. These features are admittedly not a problem in many applications of the electrode.

We have prepared an oxygen electrode that has the potential for being easily fabricated on a miniature scale and for responding more rapidly than the conventional Clark electrode. The electrode is based on a polymer bilayer coating a pair of conducting electrodes, one is the sensor electrode, the other is the reference electrode. The inner layer is a cross-linked polyelectrolyte, VTAC, that is hydrophylic and is capable of functioning as a supporting electrolyte in an electrochemical cell. The hydrophobic outer layer passes oxygen, but excludes hydrated ionic species in the sample solution. A network of oxygen-permeable poly [dimethylsiloxane] (PDMS) was used as the outer, oxygen-selective layer. Since this oxygen electrode is fabricated by simply dipping the conducting substrate into solutions of polymer and then cross-linking, fabrication on a miniature [perhaps ultramicroelectrode scale (184)] may be possible. Since the polymer films on this electrode are very thin, the response time is therefore improved. The electrode was evaluated by exposure to a series of O_2/N_2 calibration standards that were 10, 51, 107 and 498 ppm O_2. The calibration curve of electrode response vs. $[O_2]$ was linear from ambient air O_2 concentration down to 51 ppm with a precision of 2-10% RSD.

M. Conclusions

The results of our research thus far lead to the following conclusions:

(a) The formation of polymer networks by gamma irradiation is a viable means for preparing polymer-modified electrodes. This procedure is especially useful for immobilizing ionic, water-soluble polymers for subsequent use in aqueous solution.

(b) Variation in radiation dose has little effect on "permeability" of ionic polymer networks such as DDAC and VTAC, but has a large effect on non-ionic polymers such as PAN and PEI

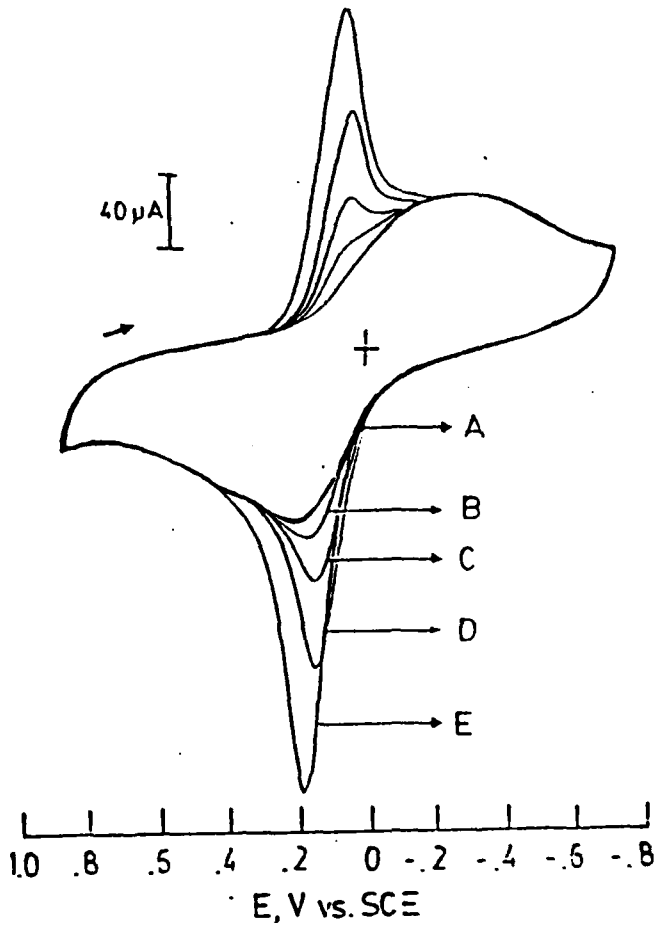


Figure 6. Steady-state cyclic voltammogram of the electrode gamma^{8}-graphite; DDAC/DCIP, 3:1 (14 microns): (A) 0.1 M NaCl, 0.1 M phosphate buffer, pH=7.0. Subsequent addition of cytochrome c: (B) 0.2 mM; (C) 0.5 mM; (D) 0.7 mM; and (E) 1.5 mM. Each of the cytochrome c voltammograms was recorded after the electrode was in solution for 5 min. The third cycle is shown. Scan rate 10 mV/s.

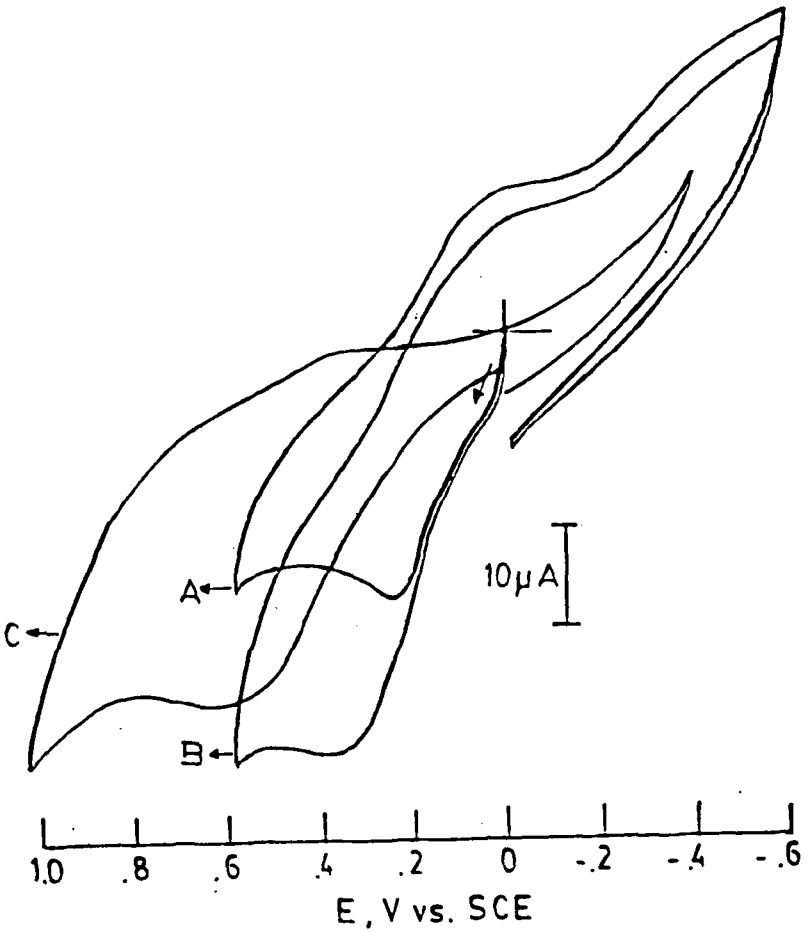


Figure 7. Cyclic voltammograms for (A) the electrode gamma^{5}-graphite;VTAC/HQ, 1:10 in 0.1 M NaCl, 0.1 M phosphate buffer, pH=6.8, (B) 2 mM NADH added to system 'A', and (C) unmodified graphite in the same NADH solution as 'B'. Scan rate is 5 mV/s.

(c) Organic redox agents can be immobilized in a network by irradiating a mixture of polymer and redox agent.

(d) Electrodes with appropriate organic redox agents exhibit catalytic acivity toward molecules such as NADH and cytochrome c.

(e) A simple oxygen electrode formed from two cross-linked networks has been demonstrated.

The greatest advantage of immobilization through gamma-irradiation is its generality; any polymer can be potentially attached to an electrode as a network through free radical cross-linking. No detailed synthetic scheme is needed. A drawback to using free radical chemistry is the potential multiplicity of products.

III. Publications and Presentations

1. Manuscripts

(1) Electrodes Coated with Polymer Networks Cross-Linked by γ-Irradiation. E.S. DeCastro, D.A. Smith, J.E. Mark, and W.R. Heineman. J. Electroanal. Chem. 138, 197 (1982).

(2) Electrodes with Polymer Network Films Formed by Gamma-Irradiation Cross-Linking. E.S. DeCastro, E.W. Huber, D. Villarroel, C. Galiatsatos, J.E. Mark, W.R. Heineman and P. T. Murray. Anal. Chem. 59, 134 (1987).

(3) Conductive Polymer-Coated Electrode as a Detector for Electroinactive Anions. Y. Ikariyama and W.R. Heineman, Proc. 2nd Int. Meeting Chemical Sensors, Bordeaux, 1986, pp. 669-672.

(4) Gamma-Irradiated Polymer-Modified Mercury Film Electrodes. M.J. Kelly and W.R. Heineman, J. Electroanal. Chem., in press.

(5) Bonding Organic Redox Agents into Polyelectrolyte Network Coatings on Electrodes by Gamma-Irradiation Cross-Linking. E.S. DeCastro, J.E. Mark and W.R. Heineman. Anal. Chem., submitted.

(6) Enzyme Electrode Directly Prepared on Graphite by Gamma-irradiation of Glucose Oxidase in a Poly(vinyl alcohol) Matrix. C. Galiatsatos, Y. Ikariyama, J.E. Mark, and W.R. Heineman. Biosensors, submitted.

2. Abstracts of Meeting Presentations

(1) Electrodes Coated with Polymer Networks Cross-Linked by Gamma-Irradiation. Symposium on Polymer Film Electrodes, 161st Meeting of the Electrochemical Society, Montreal, Canada, May 9-14, 1982. W.R. Heineman, E. DeCastro, D. Smith, and J.E. Mark. Invited lecture.

(2) Electrochemistry of Electrodes Coated with Cross-Linked Polymer Networks. 1983 International Symposium on LCEC and Voltammetry, Indianapolis, May 15-17, 1983. W.R. Heineman, D.A. Smith, E.S. DeCastro, D. Villarroel, and J.E. Mark.

(3) Characterization of Electrodes Coated with Polymer Networks Cross-Linked by Gamma Irradiation. Symposium on Mechanisms and Modeling of Electrochemical Membrane Processes, 163rd Meeting of the Electrochemical Society, San Francisco, May 8-13, 1983. W.R. Heineman, E.S. DeCastro, D.A. Smith, D. Villarroel, and J.E. Mark. Invited lecture.

(4) Cross-Linked Polymer Modified Electrodes, 15th Central Regional ACS Meeting, Oxford, Ohio, May 23-25, 1983. W.R. Heineman, E.S. DeCastro and J.E. Mark.

(5) Electrodes Coated with Polymer Networks Cross-linked by Gamma Irradiation, Working Group Meeting on Principles and Applications of Electrochemistry, Army Research Office, Charleston, S.C., December 12-15, 1983. Invited lecture.

(6) Electrodes Coated with Immobilized Redox Networks: 2,6-Dichlorophenolindophenol Bonded to Cross-Linked Poly(Diallyl Dimethyl Ammonium Chloride). E.S. DeCastro, W.R. Heineman, and J.E. Mark. ACS National Meeting, St. Louis, April 8-13, 1984. Poster.

(7) Two-Step Modified Electrodes: 2,6-dichlorophenolindophenol Bonded to Cross-Linked Poly(Diallyl Dimethyl Ammonium Chloride), 1984 International Symposium on LCEC and Voltammetry, Indianapolis, IN., June 3-5, 1984. W.R. Heineman, E.S. DeCastro, and J.E. Mark.

(8) Electrodes with Network Films Formed by Gamma Irradiation Cross-Linking. E.S. DeCastro, D.O. Villarroel, J.E. Mark and W.R. Heineman. Symposium on Polymeric and Modified Electrodes, 166th Meeting of the Electrochemical Society, October 7-12, 1984, New Orleans. Invited lecture.

(9) Electrodes with Network Films Formed by Gamma Irradiation Cross-Linking. E.S. DeCastro, J.E. Mark and W.R. Heineman. 1984 Scientific Conference on Chemical Defense Research, November 13-16, 1984, Poster.

(10) Electrodes Coated With Polymer Networks Formed by Cross-Linking With Gamma Radiation. E.S. DeCastro, D. Villarroel, C. Galiatsatos, J.E. Mark, and W.R. Heineman. Symposium on Chemically Modified Electrodes for Analytical Purposes. 1985 International Electroanalytical Symposium, May 29-31, 1985, Chicago, IL.

(11) Polypyrrole-Coated Electrode as a Detector of Ionic Substances. Y. Ikariyama and W.R. Heineman. 169th Meeting, Electrochemical Society, Boston, May 4-9, 1986.

(12) Electrochemical Characterization of Electrodes Coated with Poly(vinyl alcohol) Networks Formed by Gamma-Irradiation Cross-Linking. C. Galiatsatos, J.E. Mark, W.R. Heineman. 1986 International Electroanalytical Symposium, Cherry Hill, NJ, May 28-30, 1986. Poster.

(13) Effective Immobilization of Redox Mediators in a Poly(Vinyl Alcohol) Matrix by Using Gamma-Irradiation Cross-Linking. C. Galiatsatos, J.E. Mark, and W.R. Heineman. Symposium on Electrochemistry-Chemically Modified Electrodes. Pittsburgh Conference & Exposition, March 9-13, 1987, Atlantic City, NJ.

(14) Investigation of Enzyme Electrodes as Possible Biosensors. G.C. Barone III, C.E. Lunte and W.R. Heineman. Symposium on Electrochemistry-Chemically Modified Electrodes. Pittsburgh Conference & Exposition, March 9-13, 1987, Atlantic City, NJ.

IV. Participating Scientific Personnel

William R. Heineman, Professor

James E. Mark, Professor

Eileen Birch, postdoctoral assistant

Emory DeCastro, graduate student, Ph.D. 1984

Doris Smith, graduate student, Ph.D. 1987

Mark J. Kelly, graduate student

Dwight Blubaugh, graduate student

Louis A. Coury, graduate student

George Barone, graduate student

Christos Galiatsatos, graduate student

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